Applied Catalysis B: Environmental 97 (2010) 236–247

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

New insights into the promoting effect of H_2O on a model $Pt/Ba/Al_2O_3$ NSR catalyst

Jin-Yong Luo, William S. Epling*

Department of Chemical Engineering, University of Waterloo, Waterloo, ON N2L 3G1, Canada

ARTICLE INFO

Article history:
Received 14 January 2010
Received in revised form 22 March 2010
Accepted 9 April 2010
Available online 24 April 2010

Keywords:
Hydrogen spillover
Isocyanates
Automotive catalysis
NO_X trap
NO_X reduction

ABSTRACT

The effects of H_2O on the performance of a model $Pt/Ba/Al_2O_3$ catalyst and regeneration of the catalyst surface were investigated, both in the absence and presence of CO_2. In the absence of CO_2, an unexpected promotional effect of H_2O was observed at low temperature. For example, in the presence of H_2O, 90% NO_X conversion was obtained at 150 °C, which is the same as that at 350 °C under otherwise identical conditions. The results demonstrate that regeneration, the rate-limiting step at low temperature, occurs through hydrogen spillover to the nitrates, and not through reverse NO_X species migration to the Pt sites, and the presence of H_2O greatly promotes the hydrogen spillover rate by providing and stabilizing surface hydroxyl groups. The promotional effect of H_2O gradually decreases with increasing temperature, and shows no positive effect above 350 °C. In the presence of CO_2, however, the presence of H_2O always results in improved performance in the entire temperature range. Besides enhanced hydrogen spillover, another contribution of H_2O when CO_2 is present, is to weaken the detrimental effect of CO. CO is formed via the reverse water–gas shift reaction and poisons Pt sites as well as forms barium isocyanates. The H_2O decreases the amount of CO formed as well as hydrolyzes the –NCO species.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Lean-burn engine use, vs. today's stoichiometric-burn gasoline engines, leads to increased fuel efficiency and decreased CO_2 emissions, but the standard three-way catalyst is inefficient in reducing NO_X under the net lean exhaust conditions. NO_X storage and reduction (NSR) is one solution to reduce lean-burn engine exhaust NO_X emissions. The NSR catalysts that have been commercialized and discussed in the literature consist mainly of $Pt/Ba/Al_2O_3$, and it has been well established that the operating principle of this catalyst generally involves the following five steps [1]:

Step 1: NO oxidation on the Pt sites to NO_2;
Step 2: NO or NO_2 sorption on the barium sites in the form of solid nitrites or nitrates;
Step 3: reductant evolution at the transient from the lean to rich phase;
Step 4: solid nitrite or nitrate decomposition;
Step 5: NO_X reduction by added reductant to N_2.

NSR catalysts operate under cyclic conditions of fuel lean and rich, relative to O_2, environments. Generally, the first two steps refer to NO_X storage and occur in the lean phase, and the last three steps refer to NO_X reduction and occur in the rich phase. The main purpose of the rich phase is to remove the nitrites or nitrates by catalytic reduction thereby regenerating the storage sites for the next cycle of NO_X sorption.

H_2O and CO_2 are always present in the exhaust gas, and both influence NO_X storage and reduction. For the storage process, the effect of H_2O and CO_2 has been intensely investigated. For instance, it has been reported that the presence of H_2O and CO_2 leads to the partial formation of $Ba(OH)_2$ and $BaCO_3$ from BaO, and the reactivity between NO_X and these species decreased in the order of $BaO > Ba(OH)_2 > BaCO_3$ [2]. With respect to CO_2, there is a general consensus that it always has a detrimental effect on NO_X storage. However, in regards to H_2O, there have been different conclusions reported. For example, previous literature has shown that both H_2O and CO_2 decrease the NO_X trapping efficiency to some extent and when both H_2O and CO_2 are present, a cumulative effect can be observed at low temperature. However, at high temperature, the detrimental effect of CO_2 plays a determining role, with the effect of H_2O insignificant [3,4]. Similar findings have been demonstrated by Scholz et al. and Corbos et al. [5,6]. On the other hand, Lietti and co-workers reported that in the absence of CO_2 and at temperatures below 250 °C, H_2O has a promoting effect on NO_X storage, both prior to breakthrough being observed, i.e. under cycling conditions, as well as increasing the total amount trapped when saturation was reached. However, a negative effect was observed at higher temperature. When CO_2 was present, H_2O has been shown to increase

* Corresponding author.
E-mail addresses: wepling@chemengmail.uwaterloo.ca, wepling@cape.uwaterloo.ca (W.S. Epling).

0926-3373/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcatb.2010.04.007

NO_X storage performance prior to breakthrough, but resulted in a decrease in the total amount of NO_X stored when measuring the integral amount of NO_X adsorbed at saturation [2]. Lindholm and co-workers reported that, under cycling conditions, H_2O had a negative effect on NO_X storage in the absence of CO_2, while such an effect did not exist in the presence of CO_2. Moreover, a slight promotional effect of H_2O was observed for NO_X storage at 400 °C [7]. Recently, Chaugule et al. found both positive and negative effects of H_2O on NO_X storage, depending on the Pt and Ba loading and their interaction [8]. Unfortunately, it seems that the reasons for these results and the apparent discrepancies between studies are not fully understood.

Although there is substantial research regarding NSR catalysis, the rich-phase reactions are not well understood because the rich phase is very short, on the order of 1–5 s, and it is difficult to decouple the reductant evolution, nitrite/nitrate decomposition and NO_X reduction steps. Recently there has been more effort directed at understanding the regeneration process, since depending on operating conditions regeneration can sometimes determine overall performance. Temperature, reductant type and amount, and lean/rich times and ratio are known effects. Different types of reductant, such as H_2, CO and hydrocarbons, have been compared [9–12], and it is well established that H_2 is the most active among them. Although CO is almost as effective as H_2 at relatively high temperature, it has also been reported that H_2 could be the actual reductant involved in the regeneration reactions since it can be formed from CO via the water–gas shift (WGS) reaction [9,12]. Complicating the picture, NH_3 is often observed during the rich phase and is generally thought to be a reaction intermediate when using H_2 as the reductant [13].

It has been reported that the regeneration of the stored NO_X is the rate-limiting step for the entire NO_X storage and reduction process at temperatures below 400 °C [9]. Although models for NO_X storage have been proposed [14,15], the detailed mechanism for reductant-induced regeneration is still not well understood. One important step in regeneration, as mentioned above, is NO_X release or nitrate/nitrite decomposition. According to literature, three types of decomposition driving force have been proposed. The first is a change in the gas-phase environment that shifts the equilibrium between gas and solid phase NO_X towards decomposition of stored solid-phase NO_X; second is the heat released by exothermic reactions that decomposes the stored NO_X, especially when oxygen is available in the regeneration phase [1,16]; and third, NO_X release or nitrate decomposition can be catalyzed, which involves the participation of the reductant and precious metal sites [17,18]. These findings suggest that the first two can be dominant at high temperature, while at relatively low temperature it is more likely that the release/decomposition is a catalyzed process.

However, even with these results, there is still a lack of comprehensive understanding of regeneration, and some unresolved issues exist, even with H_2 as the reductant. For example, since this process can be a catalyzed reaction at low temperature, mass transfer or surface diffusion of reductant species or intermediates to the nitrite/nitrate site or NO_X to the reduction site can be rate-limiting, which is suggested by the observed low activation energy, approximately 16.4 kJ/mol (4 kcal/mol) for the reduction of stored NO_X by H_2 [12]. The "direction" of the diffusion/reduction process though remains unknown. Is it preceded via hydrogen spillover to the nitrates, or the reverse migration of nitrates to the Pt sites, or occurs just at the Pt and Ba interface? Under relatively more realistic cycling conditions, such as with a very short rich step on the order of 1–5 s, this diffusion may become more important, especially during the so-called cold-start period. So in order to maximize catalytic performance, a better understanding of the regeneration step is required. Furthermore, although H_2 is commonly used as a reductant, less is known about effect of H_2O and CO_2 on the regeneration process.

Keeping all these questions in mind, in this study, cycling tests were performed and the effect of H_2O and CO_2 on catalytic performance was investigated. The storage and reduction process was decoupled through targeted catalyst design and experiments, thereby resolving key issues.

2. Experimental description

2.1. Storage and cycling on monolith catalyst

The model monolith catalyst used in this study, with a cell density of 400 cpsi, was supplied by Johnson Matthey. It contains 2.0 g/in.^{3} Al_2O_3, and 1.45 wt% Pt and 20 wt% Ba relative to the Al_2O_3. The sample, with 228 cells and length of 2.4 in., was wrapped with 3 M automotive catalyst matting material to prevent gas-bypass and was positioned in a quartz-tube reactor mounted in an electric furnace. Two K-type thermocouples were placed inside the catalyst for temperature measurement at the front and back part of the catalyst. Temperature differences between the front and back were on the order of 3–4 °C. All the temperatures listed in this paper are based on the average values between these two.

All gases except N_2 were supplied by Praxair. N_2 was produced using an On-Site gas system N_2 generator. Lean and rich gases were mixed separately via Bronkhorst mass flow controllers, and the gas mixture directed to the reactor was switched by a fast-acting solenoid valve. In order to avoid flow fluctuation during switching, the pressure was maintained constant by adjusting a by-pass valve. H_2O was introduced using a Bronkhorst controlled evaporation and mixing system. All the gas lines were heated and maintained at 120 °C to prevent water condensation. The total gas flow rate was 11.2 L/min, corresponding to a gas hourly space velocity of 30,000 h^{-1}. The outlet NO, NO_2, N_2O, NH_3, H_2O, CO and CO_2 concentrations were monitored by a MKS MultiGas 2030 FTIR analyzer at approximately 2 Hz.

Before each experiment, the catalyst was exposed to at least 10 lean/rich cycles at 350 °C until no gas phase CO_2 was observed, with a lean phase composed of $NO_X/O_2/N_2$ and the rich phase composed of H_2/N_2. After that, the sample was heated to 500 °C in N_2 and then 1% H_2 was introduced for 15 min to clean and condition the sample. Finally, the reactor was cooled down in N_2 to the target temperature, and storage and cycling experiments were then performed. Unless otherwise specified, the lean-phase gas contained 360 ppm NO, 10% O_2, and a balance of N_2; and the rich phase contained 1% H_2 balanced by N_2. In investigating the effect of H_2O and CO_2, 5% of each was introduced individually or together. For the cycling experiments, an 80 s lean phase and a 10 s rich phase were used. The NO_X conversion, based on the average of three cycles in series once steady cycle-to-cycle performance was observed, was calculated as follows: (total NO_X fed – NO_X in effluent)/total NO_X fed, including NO and NO_2 from both the lean and the rich phase.

2.2. Temperature-programmed techniques with powder catalysts

The temperature-programmed experiments were performed with a Hiden CatLab reactor. The gases were analyzed by a Hiden QIC mass spectrometer. For the H_2O-TPD experiment, two model powder catalysts supplied by Johnson Matthey were used, 1%Pt/Al_2O_3 and 1.5%Pt/14%Ba/Al_2O_3. Before H_2O adsorption, 200 mg of the catalysts were pretreated in He at 500 °C for 15 min, then 5 vol% H_2O was introduced for 15 min as the temperature was decreased to ca. 60 °C. After flushing with He for 15 min, the temperature was raised and H_2O-TPD performed. For the 1.5%Pt/14%Ba/Al_2O_3 catalyst, an additional cycling pretreat-

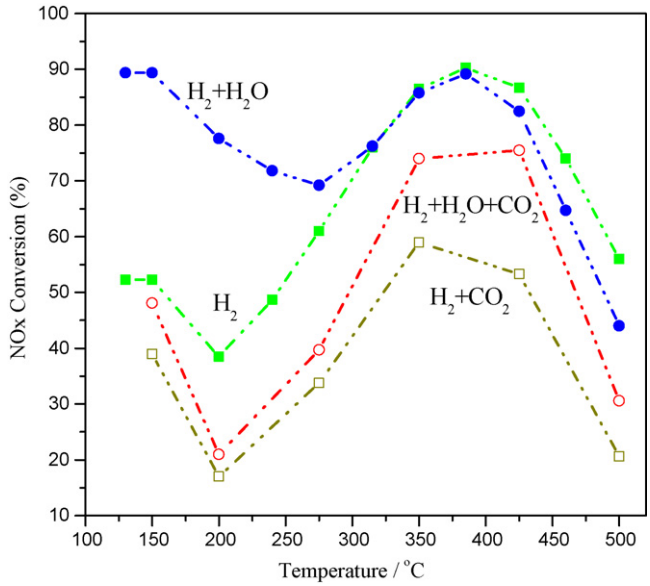

Fig. 1. NO_X conversion profiles as a function of temperature without or with 5% H_2O, 5% CO_2 individually or together (lean phase: 360 ppm NO, 10% O_2; rich phase: 1% H_2; balance N_2).

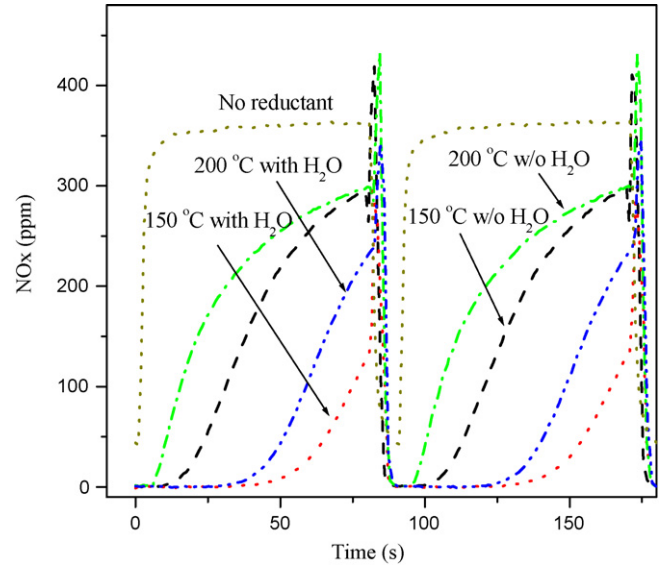

Fig. 2. NO_X outlet concentration profiles vs. time during cycling experiments at 150 and 200 °C with or without 5% H_2O (lean phase: 360 ppm NO, 10% O_2; rich phase: 1% H_2; balance N_2).

ment at 350 °C using 360 ppm NO_X, 10% O_2 and 1% H_2 in the lean and rich phases, respectively, was performed in order to remove the surface carbonates. All gas flow rates were fixed at 95 ml/min.

For the H_2-TPR experiment, 200 mg 1.5%Pt/14%Ba/Al_2O_3 was first reduced in 5% H_2/He at 450 °C, then NO_X adsorption (360 ppm) was performed at 200°C for 30 min. After flushing with He and decreasing the temperature to 60 °C, H_2-TPR was performed with 1% dry H_2 or 1% H_2 containing 5% H_2O. Meanwhile, the same experiment was performed with a Pt/Ba$(NO_3)_2$ catalyst (1 wt.% Pt, 25 mg) but without the pretreatment for NO_X adsorption. The Pt/Ba$(NO_3)_2$ catalyst was prepared by impregnation of crystalline Ba$(NO_3)_2$ with a $(NH_3)_4Pt(OH)_2$ solution and drying at 70 °C overnight. Both chemicals were purchased from Alfa Aesar.

3. Results and discussion

3.1. Overall catalytic performance

NO_X conversions as a function of temperature during cycling conditions using H_2 as the reductant, in the presence and absence of H_2O and/or CO_2, are shown in Fig. 1. For H_2 alone, as the temperature was increased from 200 to 385 °C, the conversion monotonically increased from 40% to 90%. However, further increasing the temperature to 500 °C led to decreased conversion. This trend as a function of temperature is typically noted in the literature. First, since NO oxidation and reduction are promoted by temperature, increasing the temperature above 200 °C typically results in improved performance, but due to thermodynamic limitations at high temperature, the stored NO_X tends to decompose, leading to a decrease in NO_X storage and therefore overall NO_X conversion. The maximum conversion was observed at 385 °C, consistent with the optimum value of 380 °C reported in previous literature [19]. Worth noting is that at low temperature, between 130 and 150 °C, a 52% conversion was observed, higher than that at 200 °C. Previous work [20] also found that performance is better at 135 °C than at 200 °C using H_2 as the reductant. The reason for such a trend will be discussed below.

With the introduction of H_2O, unexpected improvement in conversion was observed at the lower temperatures. For example, 90% conversion was achieved even at 130 and 150 °C, the same as that at 350 °C under otherwise identical conditions. It should be noted that a relatively high selectivity towards NH_3 was observed at lower temperatures (at 150 °C for example, for each cycle 128 μmol NH_3 was released in the presence of H_2O, and 56.7 μmol NH_3 in the absence of H_2O). Many commercial systems utilize a downstream SCR catalyst to promote higher conversions, and the NH_3 formed can be stored on the downstream SCR catalyst for NO_X reduction in the subsequent lean phase in such a system [21]. The data demonstrate that the effect of H_2O on conversion is especially sensitive to temperature. As the temperature was increased to 275 °C, the promotional effect of H_2O decreased. Between 300 and 385 °C, there was no difference between the experiments with and without H_2O. At temperatures above 385 °C, the addition of H_2O resulted in a negative effect.

The inclusion of CO_2 in the feed significantly inhibited NO_X conversion over the entire temperature range. However, the co-presence of H_2O always resulted in improved performance relative to the dry experiments with CO_2. The improvement was especially significant between 350 and 425 °C, with 15% and 20% higher conversions, respectively.

Based on these results, the following questions were raised:

1. In the absence of CO_2, why does H_2O promote NO_X conversion to such a great extent at low temperature?
2. Why is the activity better at 150 °C compared to that at 200 °C?
3. In the presence of CO_2, why does H_2O always promote NO_X conversion, especially between 350 and 400 °C, whereas at the same temperature, no promotional or even a slightly detrimental effect of H_2O can be observed in the absence of CO_2?

3.2. Promoting effect of H_2O at low temperature

3.2.1. Effect of H_2O on the storage process

The outlet NO_X concentration profiles during cycling at 150 and 200 °C, both with and without H_2O, are shown in Fig. 2. It is clear that H_2O promotes better NO_X conversion at both temperatures. Generally, NO oxidation is considered the first, and key step for efficient NO_X storage. But it is well documented that H_2O inhibits NO oxidation [5]. Also, NO oxidation rates should increase between 150 and 200 °C, and therefore it is apparent that the improved performance at 150 °C is not related to NO oxidation.

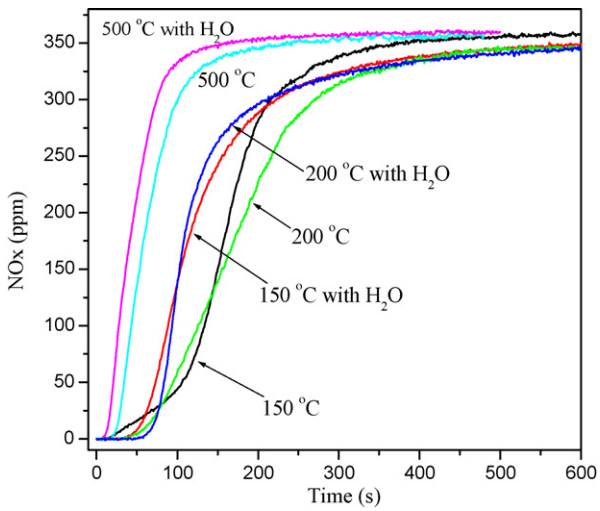

Fig. 3. NO_X outlet concentration profiles vs. time during storage at 150, 200 and 500 °C with or without 5% H_2O (360 ppm NO, 10% O_2, balance N_2).

The data presented in Figs. 1 and 2 were obtained under cycling conditions, in which both the storage and regeneration can be limited by each other, which complicates the analysis. To decouple the storage and reduction process, further NO_X storage experiments were performed, with and without H_2O, where the catalyst was saturated with NO_X in a single lean-phase event, following the cleaning at 500 °C described in the experimental methods section. The outlet NO_X concentration profiles during storage are displayed in Fig. 3. Under these conditions, it is clear that H_2O caused a decrease in the total amount of NO_X stored. At least three reasons can be proposed for the decreased storage performance. First, as was mentioned above, the presence of H_2O suppresses NO oxidation, which is a key step for storage. Second, NO_X adsorption on the Al_2O_3 surface can be substantial at low temperature, and H_2O greatly suppresses the amount of NO_X adsorbed on Al_2O_3 [22]. Third, competitive adsorption between H_2O and NO_X for the barium sites is also possible. The overall observation is consistent with previous literature, which shows that H_2O decreases the NO_X storage capacity to an appreciable extent [4,6,7]. Although the total NO_X stored decreased, it is apparent that in the presence of H_2O, the NO_X breakthrough time (first evidence of NO_X in the outlet gas after the onset of the lean phase) is slightly longer, both at 150 and 200 °C. Such a H_2O-induced enhancement in breakthrough time was also observed by Lietti et al. [2], and they proposed it might be associated with participation of surface hydroxyl species in the storage process. Other studies [23,24] have shown the H_2O-induced leaching or redistribution of barium species on Al_2O_3, which may also result in the slightly improved NO_X uptake.

Still, such a slight improvement in storage, in terms of breakthrough time and NO_X trapped at that time, cannot account for the enhanced NO_X conversion in the presence of H_2O observed during the cycling experiments. To prove this, the lean-phase time during cycling conditions was changed and conversions measured, shown in Fig. 4(a), and the NO_X reduction performance was better in the presence of H_2O for the three different lean times tested. But it is clear from Fig. 3 that during the saturation experiment, the amount stored after 120 s was still lower in the presence of H_2O (365 μmol in the absence of H_2O vs. 338 μmol in the presence of H_2O both at 150 and 200 °C).

The total amounts of converted NO_X for the different lean times, under cycling conditions, were calculated and the results are shown in Fig. 4(b). In general, the longer lean time should result in more stored NO_X in the sample, and therefore can correspond to an increased amount of converted NO_X if the amount of

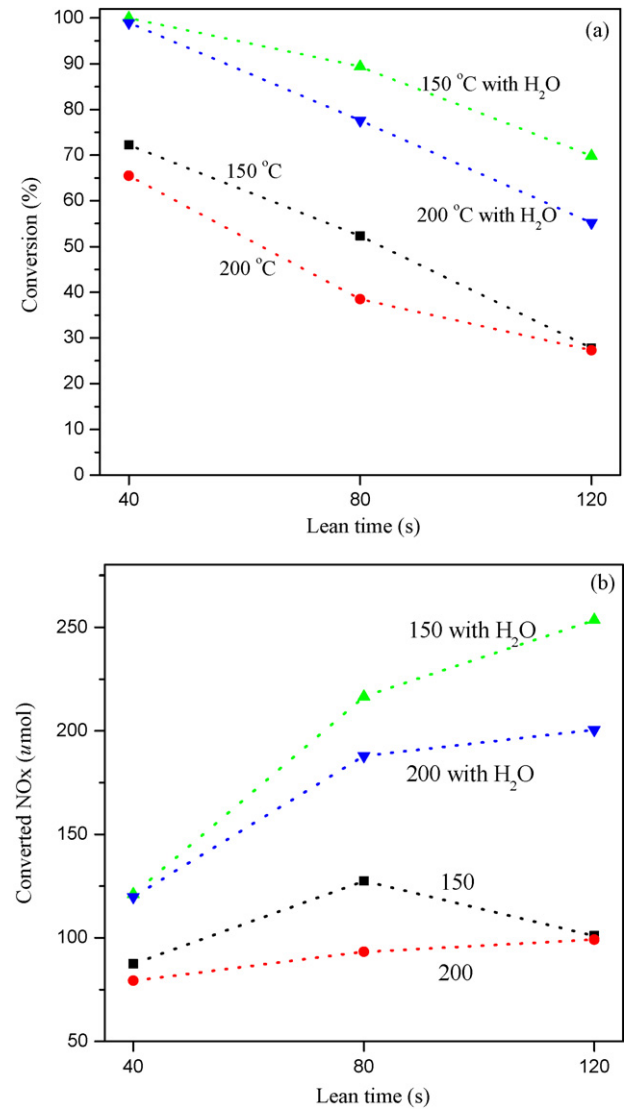

Fig. 4. NO_X conversion profiles (a) and converted NO_X amount (b) of different lean time 40, 80 and 120 s at 150 and 200 °C with or without 5% H_2O (lean phase: 360 ppm NO, 10% O_2; rich phase: 1% H_2; balance N_2).

reductant added during the regeneration phase is sufficient. This was observed for all cases except at 150 °C without H_2O where, as the storage time increased from 80 to 120 s, less NO_X (around 100 μmol) was converted. However, the decreased amount of converted NO_X was not due to a larger amount of NO_X released and unconverted in the rich phase, since the puff during switching to the rich phase did not show much difference. It is more likely that less NO_X was converted although the residual amount of NO_X contained in the sample is thought to be larger. In other words, although sufficient reductant is added, inefficient regeneration occurs as will be shown and discussed below.

These combined results clearly show that, at low temperatures, no consistent correlation can be made between the observed improved performance and the NO_X storage process. It therefore must be related to the regeneration or reduction process, with it being promoted by the presence of H_2O.

3.2.2. *Promotional effect of H_2O on the regeneration process*

In order to further understand the importance of H_2O, as well as H_2, the effect of H_2 and H_2O concentration on NO_X conversion was investigated, and the results are displayed in Fig. 5(a) and (b). In

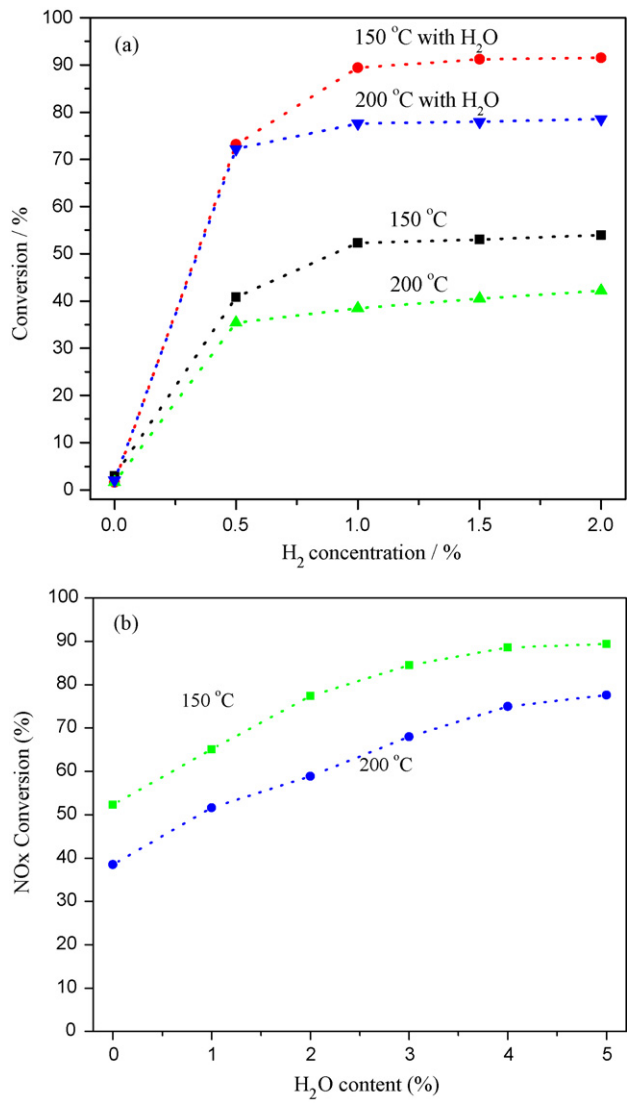

Fig. 5. NO_X conversion profiles vs. H_2 (a) and H_2O (b) concentration at 150 and 200 °C. (a: lean phase: 360 ppm NO, 10% O_2, 5% H_2O; rich phase: 1–5% H_2, 5% H_2O; balance N_2; b: lean phase: 360 ppm NO, 10% O_2, 1–5% H_2O; rich phase: 1% H_2, 1–5% H_2O; balance N_2.)

the presence of 5% H_2O, increasing the H_2 concentration from 0 to 1% resulted in very obvious improvement in performance, but further increasing H_2 to 5% had very limited effect. This suggests that 1% H_2 for 10 s was enough to regenerate most of the actively participating sample at steady cycle-to-cycle conditions. These data do not suggest that all the nitrate species were regenerated simply because sufficient H_2 is introduced. Using DRIFTS, Ji et al. found that a large fraction of formed nitrates are not decomposed during cycling experiments and do not participate in NO_X abatement under steady cycle-to-cycle conditions [25]. On this basis, the H_2 concentration was kept at 1%, and the effect of H_2O concentration was studied. As shown in Fig. 5(b), increasing the H_2O content from 0 to 5% monotonically promoted higher NO_X conversion.

As was mentioned in the introduction, at low temperature, NO_X regeneration is catalytically activated, involving the reductant, solid barium nitrate and reaction over the active Pt sites. For such a process, mass transfer, or surface diffusion, is an important factor. Literature evidence shows that the reduction of NO by H_2 can be accomplished at temperatures as low as 60 °C over a Pt-Ba/Al_2O_3 catalyst [13]. Tests with the catalyst used in this study show that complete NO conversion can be obtained at 100 °C with NO and H_2 introduced simultaneously in the gas phase (data not shown), further suggesting such a mass transfer limitation or resistance during the rich phase. In explaining the phenomena observed during cycling [3], two types of barium species have been proposed, one which is in proximity to Pt and the other not. It is expected that for the barium species proximal to Pt, regeneration is easier due to direct interaction with Pt and/or the short distance for surface diffusion. While for the other barium species, regeneration would be limited by such diffusion resistance. The data presented above suggest that H_2O may promote mass transfer in this situation.

Two models or directions of mass transfer can be proposed for NO_X trap regeneration: the first is the migration of nitrate species (via a barium nitrate transfer mode) to the Pt sites for its reaction with the reductant. This is consistent with previous work indicating that barium nitrates are extremely mobile even at temperatures below 130 °C [26]. Also, during the decomposition of barium nitrates, it has been proposed that NO_X species diffuse very efficiently to the Pt interface, which makes this process similar to homogenous catalysis [27]. The other direction is the spillover of hydrogen from the Pt sites to the barium nitrate sites [28]. In the reduction of CoO_X species during H_2-TPR [29,30], the presence of a small amount of noble metals like Pt, Pd and Rh can greatly promote this process, via activation of the hydrogen molecule and then spillover from the metal to the oxides. It is possible that the same mechanism is also involved in reduction of barium nitrate species. Very recently, both routes of reduction have been proposed, but it was concluded that debate still exists on the direction of spillover and the spillover species during the regeneration of stored NO_X [31]. Using TPSR (temperature-programmed surface reduction) and ITRM (isothermal transient response method), Lietti et al. found that H_2O greatly enhanced the reduction of stored NO_X by H_2, and almost complete reduction could be observed at temperatures as low as 100 °C [13]. This is consistent with the results during cycling conditions presented above. They proposed that H_2O promoted the rate of hydrogen spillover, but enhanced mobility of barium nitrates in the presence of H_2O was not excluded.

The challenge is to decouple the two types of migration processes. In terms of enhanced hydrogen spillover, if H_2O mainly promotes the surface diffusion rate of the hydrogen atoms, for NSR catalysts this would be over the support Al_2O_3. To decouple the two directions, an experiment was designed to investigate the effect of H_2O on the reduction of a Pt/Ba$(NO_3)_2$ catalyst by H_2, in which the support Al_2O_3 is eliminated, in order to decouple hydrogen spillover over the support. For comparison, we also performed the H_2-TPR experiments with the Pt/Ba/Al_2O_3 catalyst.

The H_2-TPR profiles with the Pt/Ba/Al_2O_3 catalyst are shown in Fig. 6(a). The sample was first reduced in 5% H_2/He at 450 °C, and then NO_X adsorption was performed at 200 °C for 30 min. After cooling further, the H_2-TPR experiment was then performed. A H_2 consumption peak, corresponding to the reduction of stored NO_X by dry H_2, is apparent at 115 °C. However, in the presence of H_2O, a H_2 consumption peak is apparent at a much lower temperature, ~63 °C, which was the temperature where H_2 was introduced, so it could have occurred at an even lower temperature. This demonstrates that H_2O promoted the reduction of stored NO_X, shifting its reduction temperature by more than 50 °C, providing further consistency in regards to the cycling data discussed above. The H_2-TPR profiles for the Pt/Ba$(NO_3)_2$ catalyst, i.e., without the Al_2O_3 support, are shown in Fig. 6(b). A H_2 consumption peak is observed at ~150 °C, corresponding to the reduction of Ba$(NO_3)_2$. It is also evident that there is little difference between the profiles in the presence or absence of H_2O. This indicates that the mobility of barium nitrates was probably not enhanced by H_2O, and therefore it is clear that hydrogen spillover via the support Al_2O_3 to the nitrates is the actual reaction route for NO_X reduction, and H_2O promotes the hydrogen spillover rate.

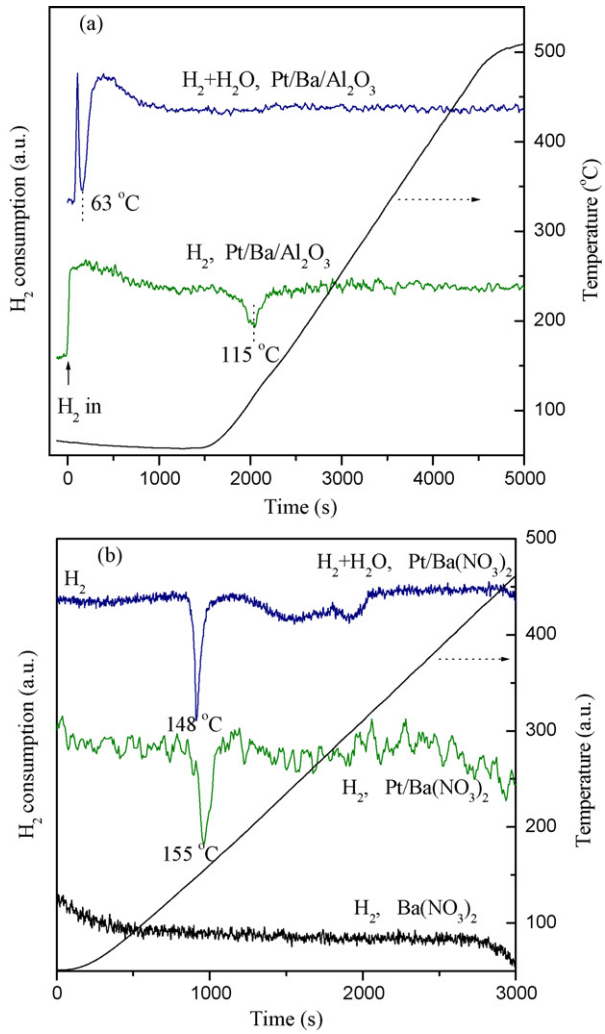

Fig. 6. H_2-TPR profiles for NO_X stored on $Pt/Ba/Al_2O_3$ (a) and $Pt/Ba(NO_3)_2$ (b) powder catalysts with or without H_2O.

In further detail, the spillover process can be described as follows. First, H_2 dissociates on Pt sites into H atoms, and then H atoms diffuse from the interface between Pt and Al_2O_3 to the Al_2O_3 surface. After surface diffusion on the Al_2O_3 surface, H atoms reach the interface between barium nitrates and Al_2O_3. As a result, spillover can result in a long-range effect, and the barium nitrates far away from Pt sites can be regenerated. That is the intrinsic reason that H_2 is always reported to be the most effective reductant for NSR catalysts. However, the range of surface diffusion can be different, depending on the relative energetics of transport, or the interaction between the hydrogen and the support, such as Al_2O_3. If no H_2O is present, it can be expected that the energetics for the transportation of hydrogen, via breaking the OH group and the formation of a new adjacent OH, is quite high, and it is very possible that a new bond between spillover hydrogen and the surface oxygen atom of Al_2O_3 will form first, in order to generate a surface layer of hydroxyl groups. Using the ITRM method, Lietti et al. found that an induction period was observed for the reduction of NO_X at 150 °C by dry H_2 [13]. From their data, it can be deduced that the induction time is actually used for the development of the surface hydroxyl groups. After the formation of these surface hydroxyls, they then serve as a "bucket brigade", to facilitate the surface diffusion of hydrogen [32], via the much weaker interaction between H atoms and OH groups. In this situation, the hydrogen atoms migrate over the surface OH groups, with the energetics being much smaller, and much faster hydrogen spillover can be attained. On this basis, the main function of H_2O is actually to form and stabilize the surface OH groups, and it can be considered as a co-catalyst for the reduction of NO_X by H_2. Therefore, if H_2O is present, the induction time would be eliminated. This is especially important under more realistic cycling conditions with a very short rich time. In Fig. 7, a schematic illustration of the reduction process is presented, in which the H_2O-generated surface hydroxyl groups facilitate hydrogen spillover, contributing to the efficient reduction of the barium nitrate sites far away from Pt centers. Consistent with our results, similar observations can be found elsewhere [32,33], with H_2O considered an efficient co-catalyst for the reduction process of other compounds by H_2, especially at low temperature. How the stored nitrates are being reduced by the spillover H and whether Pt is necessary for this step still needs further investigation.

Although H_2O has a significant promoting effect on the regeneration of stored NO_X at low temperature, as the temperature gradually increases, H_2O tends to desorb from the surface, resulting in a decrease in surface OH group concentration and therefore NO_X reduction. The data support this since increasing the temperature to 275 °C, as shown in Fig. 1, resulted in decreased performance when testing with H_2 and H_2O in the regeneration gas. This suggests that the activity is quite sensitive to H_2O, as well as temperature, indicating the importance of surface diffusion at relatively low temperature, especially under dynamic cycling conditions. However, as the temperature was further increased, exceeding 275 °C, the conversion increased. Since the same trend was observed during the experiment with dry H_2, data shown in Fig. 1, at these higher temperatures, the promotional effect of H_2O is not evident. This is because less adsorption of H_2O on the surface occurs. The reactivity increased due to increasing temperature, leading to increased NO oxidation during the lean phase and nitrate decomposition during the regeneration phase.

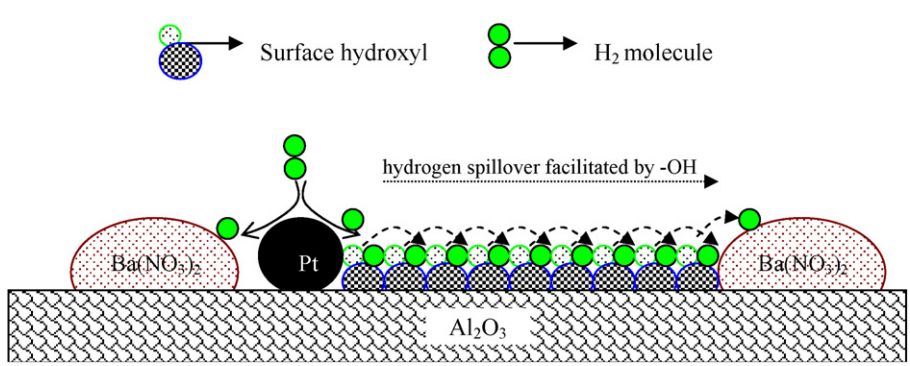

Fig. 7. Schematic illustration of the OH-promoted hydrogen spillover for the reduction of $Ba(NO_3)_2$ far away from Pt sites.

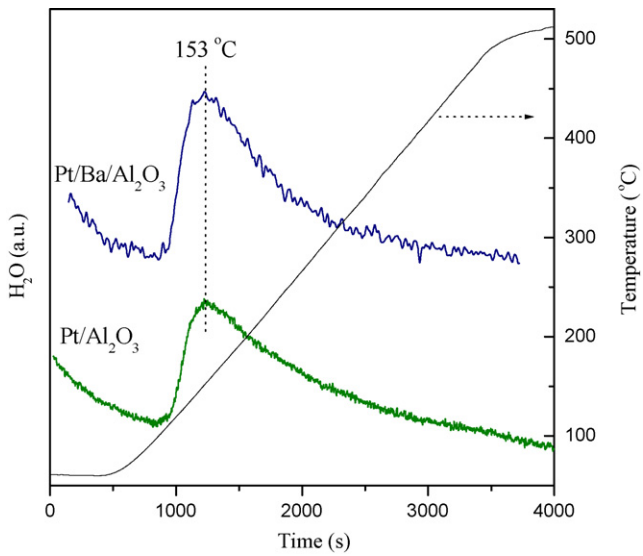

Fig. 8. H_2O-TPD profiles on Pt/Al_2O_3 and $Pt/Ba/Al_2O_3$ powder catalysts.

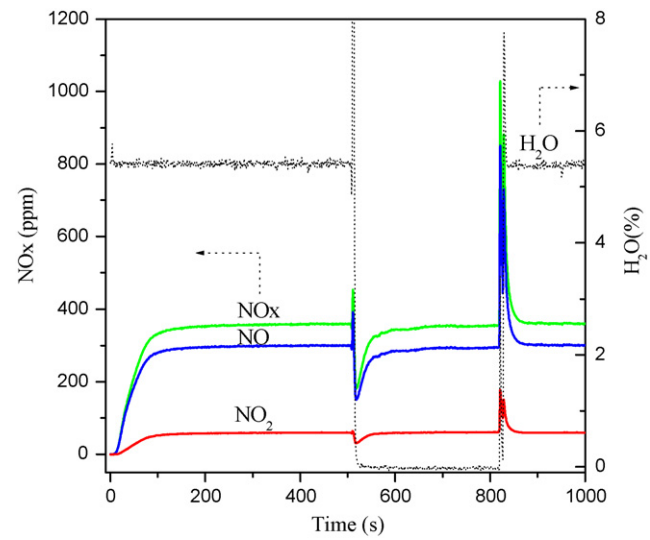

Fig. 9. Effect of H_2O on the NO_X storage and release behaviours at 500 °C. (In the presence of 360 ppm NO, 10% O_2, 5% H_2O, turn off and on again 5% H_2O).

This reasoning can be applied to explain the NO_X conversion being higher at 130 °C or 150 °C compared to 200 °C both in the presence and absence of H_2O, namely, the desorption of H_2O. Using H_2 as reductant, H_2O will inevitably be produced. This would promote hydrogen spillover and subsequent nitrate decomposition and ultimately NO_X destruction. However, the desorption of product H_2O is rapid at 200 °C, leading to the observed decrease in activity, which can be confirmed by the H_2O-TPD results shown in Fig. 8. H_2O desorbs quickly at temperatures above 150 °C, both from Pt/Al_2O_3 and $Pt/Ba/Al_2O_3$. The similar desorption profiles for both catalysts suggests that H_2O is mainly adsorbed on the Al_2O_3 surface. Additionally, at 150 °C without H_2O, the increase in the lean time from 80 to 120 s resulted in a decreased amount of converted NO_X, although more NO_X was thought to be contained on the sample. This can be attributed to that longer lean time resulting in longer exposure to NO_X, but more surface hydroxyl groups on the alumina are eliminated by NO_2 [34], with the formation of nitrite or nitrate species, leading to the decreased surface diffusion of hydrogen species during regeneration. Therefore, at low temperature surface diffusion of reductant on the support is critical for NO_X removal, having a more significant impact than on the storage process, and H_2O, or surface hydroxyl groups, greatly facilitates the hydrogen spillover during regeneration.

At very high temperature, such as 500 °C, H_2O had a negative effect on the NO_X reduction performance. This is reasonable since, first, at high temperature the regenerative reduction of the stored NO_X is relatively easy, and nitrates decompose releasing NO_X due to the gas environment change or thermal decomposition [1]. At such temperatures, NO_X performance therefore mainly depends on the NO_X storage performance. As shown in Fig. 3(b), the addition of H_2O decreased the NO_X storage capacity at 500 °C, leading to the decreased NO_X conversion. The decreased NO_X storage capacity is not due to the decreased NO oxidation ability, since after storage reaches saturation, the NO_2 concentration is the same as the thermodynamic equilibrium value 60 ppm, both in the presence and absence of H_2O, so there is available NO_2. Also, NO_X storage on Al_2O_3 is unstable at this temperature [7]. Therefore, it is likely due to competition between H_2O and NO_X for barium sites. As shown in Fig. 9, when the saturation adsorption at 500 °C was achieved in the presence of H_2O, a sudden H_2O shut-off resulted in appreciable NO_X storage again, while the sudden introduction of H_2O gave rise to fast NO_X release, supporting this conclusion.

In summary, the catalytic performance for NO_X destruction at low temperature is restricted by the regeneration. The first step during regeneration, nitrate decomposition, is impacted by hydrogen spillover, which is activated on Pt sites and the hydrogen migrates to the solid nitrate phase over the support. The migration of hydrogen can be limited by its strong interaction with the support. If H_2O is present, the pre-adsorbed OH group can serve as a "bucket brigade", thus facilitating the hydrogen spillover and greatly improving the catalytic performance, even at 150°C. As the temperature is increased, H_2O desorbed from the surface, leading to a decreased promotional effect. At very high temperature, due to thermodynamic limitations, storage determines the performance. Since H_2O decreases the NO_X storage capacity via competitive adsorption on barium at these temperatures, a slightly detrimental effect was observed.

3.3. *The detrimental effect of CO_2*

In the presence of CO_2, H_2O promoted catalyst performance across the entire temperature range. This is different from the case with no CO_2, in which H_2O had a negative effect at high temperature, indicating different mechanisms are possibly involved. To further understand the beneficial effect of H_2O, the detrimental effect of CO_2 was examined.

NO_X storage experiments, with and without CO_2, were performed at both 150 and 350 °C, and the results are shown in Fig. 10. Regardless of the presence of H_2O, CO_2 significantly decreased the NO_X storage capacity. Both a kinetic and thermodynamic limitation can be proposed for such a decrease. The kinetic aspect would be the competing adsorption of CO_2 with NO_X for barium sites, with the temporary formation of $BaCO_3$, which acts as a barrier for the diffusion of barium nitrates [15]. But for such a limitation, the total adsorption amount should not change since the carbonates will be slowly replaced by nitrates, resulting in the same storage, but over a longer time. For example, Olsson and co-workers reported that at 200 °C, total storage after 60 min using $NO_2 + O_2$ was similar when introducing CO_2 and H_2O although the initial total uptake of NO_X was decreased [35]. With a thermodynamic limitation, some portion of the barium nitrates, if they are formed, can be replaced by carbonates via CO_2, or some $BaCO_3$ species will not decompose due to the presence of CO_2 in the gas phase. Seemingly, the replacement of nitrates by carbonates is impossible based on thermodynamic calculations [2]. However, experimental results demonstrate the

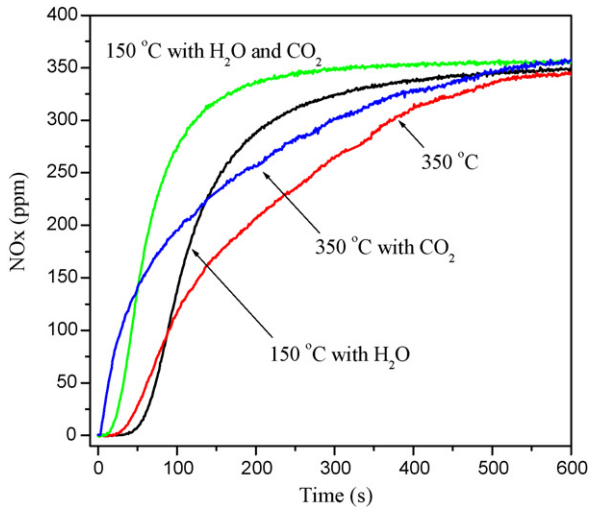

Fig. 10. NO_X outlet concentration profiles vs. time during storage at 150 and 350 °C with or without 5% CO_2. (360 ppm NO, 10% O_2, balance N_2).

replacement of barium nitrates by carbonates via CO_2, with the results shown in Fig. 11(a) and (b). When the CO_2 supply was turned off after the storage reached saturation at 350 °C in the presence of CO_2, further and substantial NO_X storage was observed. When the CO_2 was turned on again, large amounts of NO_X were released, suggesting the replacement of nitrates by carbonates. Similarly, after storage reached saturation at 350 °C in the absence of CO_2, and N_2 was introduced until the outlet gas-phase NO_X concentration decreased to very low values (less than 5% of the initially input NO_X), the introduction of CO_2 led to rapid and substantial NO_X release, suggesting that again a portion of the barium nitrates are replaced by carbonates. The CO_2-induced nitrate decomposition and NO_X release was identified previously and interpreted in terms of: $CO_{2,gas} + {}^{*}NO_{2,stored} \leftrightarrow {}^{*}CO_{2,stored} + NO_{2,gas}$ [36]. Thermodynamic calculations were performed for the following reactions at 350 °C (HSC Chemistry, Ver. 4.1, Outokumpu Research Oy, Pori, Finland), and the results are listed in Table 1. Although these calculations have been carried out based on crystalline $Ba(NO_3)_2$ and $BaCO_3$, it can provide useful information about the complex catalytic system in which possibly only the surface non-crystalline species are involved.

$$Ba(NO_3)_2 + CO_2(g) = BaCO_3 + 2NO(g) + 3/2O_2(g) \quad (R1)$$

$$Ba(NO_3)_2 + CO_2(g) = BaCO_3 + 2NO_2(g) + 1/2O_2(g) \quad (R2)$$

$$Ba(NO_3)_2 + CO_2(g) = BaCO_3 + 0.8NO(g) + 1.2NO_2(g) + 0.9O_2(g) \quad (R3)$$

The stoichiometry of (R3) was based on experimental observations of the outlet NO and NO_2 concentrations at 350 °C. It can be seen that under standard conditions (1 atm pressure of each gas-phase species), these reactions can not take place at 350 °C, while under "realistic" conditions (5% CO_2, 10% O_2, 140 ppm NO, 220 ppm NO_2), all of them become thermodynamically favorable. So at the least, the thermodynamic driving force can play a role during trapping.

Table 1
Thermodynamic calculations (ΔG, kJ/mol) for reactions (R1)–(R3).

Reaction	$\Delta_r G^\theta(350)$	$\Delta_r G(350)$[a]
(R1)	93.48	−0.85
(R2)	71.70	−6.01
(R3)[b]	80.41	−3.83

[a] $\Delta_r G(350) = \Delta_r G^\theta(350) + 2.303RT\,lgQ_r$, $Q_r = ([P_{NO_X}/P^\theta]^a[P_{O_2}/P^\theta]^b/[P_{CO_2}/P^\theta])$, (5% CO_2, 10% O_2, 140 ppm NO, 220 ppm NO_2).
[b] The stoichiometry was based on the experimental observations of the NO and NO_2 concentration at 350 °C.

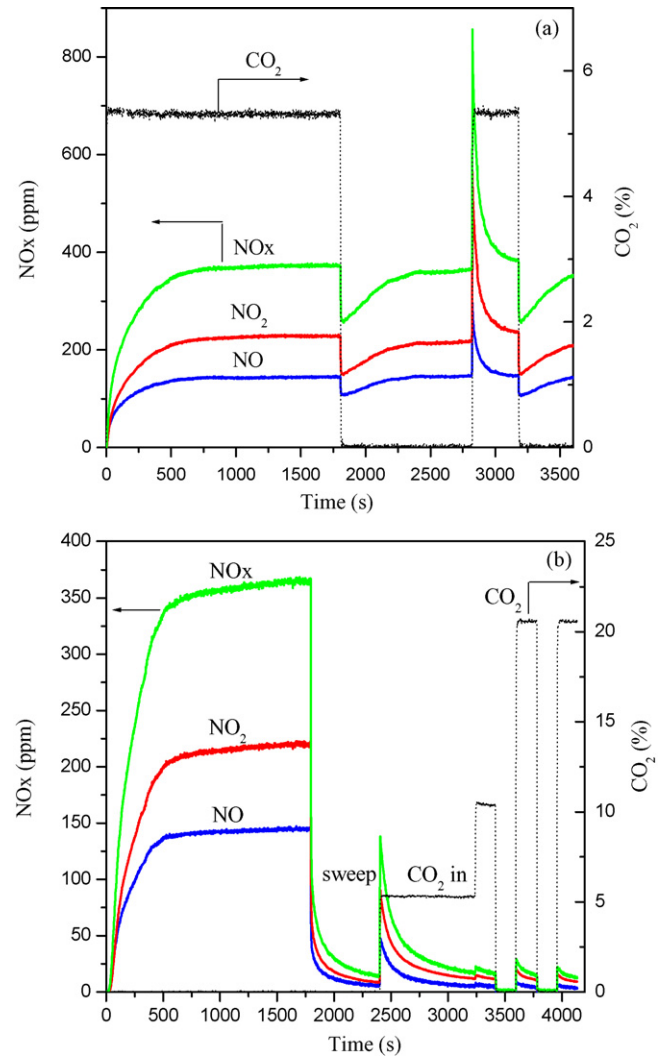

Fig. 11. Effect of CO_2 on the NO_X storage and release behaviours at 350 °C: (a) in the presence of NO_X, turn off or on 5% CO_2, (b) after storage saturation and flushing with N_2, turn on or off different concentrations of CO_2 (storage condition: 360 ppm NO, 10% O_2, with or without CO_2, balance N_2).

On the other hand, according to Letti et al. [13] the regeneration process is reported to be greatly suppressed by the presence of CO_2. In their ITRM experiments, it was found that after a known amount of NO_X was stored at 350 °C, the reduction efficiency at 200 °C exceeded 95% using H_2 as a reductant in the presence of H_2O, while it decreased to about 50% after introduction of CO_2. The detrimental effect of CO_2 gradually decreased with increasing temperature. The explanation proposed was that the Pt sites were blocked by carbonyls formed by the reverse water–gas shift reaction (RWGS). With respect to the cycling experiments here, although NO_X storage is also greatly suppressed by CO_2, it is very possible that the regeneration is also inhibited by CO_2. In comparing the cycling performance at 150 °C using $H_2 + H_2O$ and $H_2 + H_2O + CO_2$ in Fig. 1, a nearly 40% drop in conversion occurs in the presence of CO_2. The data obtained in this study showed CO was indeed produced, especially at temperatures above 200 °C. For example, 70 and 150 ppm CO were detected at 275 °C in $H_2 + H_2O + CO_2$ and $H_2 + CO_2$ conditions, respectively. Although almost no CO was detected at 150 °C in this cycling experiment, it is expected that CO can be formed

and adsorbs on the Pt even at 150 °C, supported by results of FTIR experiments [13], in which it was found that Pt-carbonyls can be formed at this temperature in a CO_2/H_2 mixture. So the poisoning effect of CO could play an important role. This poisoning effect of CO has also been previously studied in cycling conditions [10], and significant performance loss was observed at low temperature.

In summary, CO_2 greatly inhibited both the storage and reduction processes, leading to significantly decreased catalytic performance. Decreased storage can be attributed to both kinetic and thermodynamic reasons, whereas the regeneration is inhibited by the poisoning of CO on the Pt sites, which is formed from RWGS reaction between CO_2 and H_2.

3.4. *The promoting effect of H_2O in the presence of CO_2*

Although the presence of CO_2 decreased catalytic performance, the co-presence of H_2O promoted activity to some extent. Similar to the experiment with no CO_2, the promotional effect of H_2O at low temperature can be attributed to the enhanced transport of spillover hydrogen and the resulting more efficient regeneration. Coincidently, it is possible that CO is produced by the RWGS reaction and can poison Pt sites, but the presence of H_2O, as a product of RWGS, inhibits this reaction and formation of CO, weakening its poisoning effect to some extent. However, the extent of H_2O promotion is not as obvious at low temperatures, indicating the detrimental effect of CO_2 plays a determining role. Also, at temperatures above 350 °C, a gradually increased detrimental effect of H_2O was observed in the absence of CO_2, whereas in the presence of CO_2, an obvious promotional effect was observed. At these relatively high temperatures, the poisoning effect of CO on Pt sites can be excluded.

The NO_X profiles during cycling conditions at 350 and 425 °C in the presence of CO_2, with and without H_2O, are compared in Fig. 12 (a) and (b). Also, data from an experiment without reductant are included. Clearly, when no reductant was introduced, there was no NO_X release peak during the transient from lean to rich at 350 °C, whereas very obvious NO_X release peaks were observed at 425 °C. These results indicate that NO_X release by a change in the gas environment can take place only at the higher temperatures, further suggesting that NO_X is more probably released by a catalytic process at low temperature. Worth noting is that in the case when CO_2 was added, but no H_2O, an additional NO_X peak was observed immediately at the switch from the rich to lean phase. It was confirmed that this feature is not related to flow fluctuation during switching since the pressure remains constant during switching, and this peak does not appear in other experiments. Generally, a NO_X release peak can be observed when the gas is switched from the lean to rich phase when reductant is added in the rich phase mixture, with O_2 and NO absent, or as noted above, at higher temperatures with the simple removal of NO and O_2 and the resulting change in environment. However, NO_X release at the switch from rich to lean has rarely been reported. In the literature, a second N_2 peak has been reported at this phase transition [37], and this has been attributed to the reaction between the entering NO_X in the lean phase with the adsorbed ammonia formed in the rich phase.

This NO_X release peak is caused by the presence of CO originating from the RWGS reaction. Results from a cycling experiment using only dry CO (1%) as reductant are shown in Fig. 12(c). Clearly, a large NO_X release peak was formed during the switch from the rich to lean phase. Also, the NO concentration during the lean phase remained almost constant, while the NO_2 concentration increased monotonically.

Such a release peak is not likely due to CO poisoning of Pt sites at such high temperature. Even if some CO is adsorbed on the Pt surface during the rich phase, it will react with the NO_X or O_2 from the lean phase after switching, and the result will be reduction to

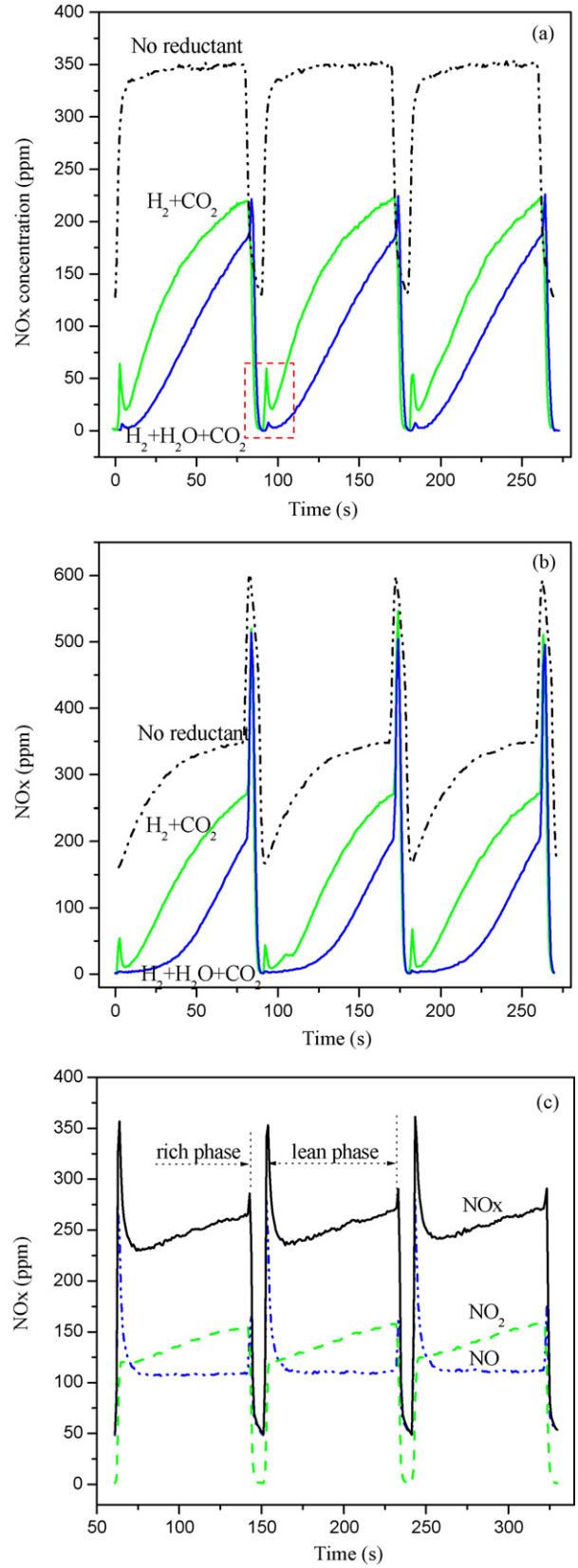

Fig. 12. NO_X outlet concentration profiles vs. time during three consecutive cycles at (a) 350 °C and (b) 425 °C using H_2 as reductant in the presence of CO_2 or $H_2O + CO_2$ (lean: 360 ppm NO, 10% O_2, 5% CO_2; rich: 1% H_2; balance N_2), (c) 350 °C using only CO as reductant (lean: 360 ppm NO, 10% O_2; rich: 1% CO; balance N_2).

N_2 and the NO_X slip profile would indicate complete NO_X uptake. Using DRIFTS techniques, two groups have detected the presence of isocyanate species (–NCO) on the catalyst surface when using CO as the reductant for stored NO_X [11,38]. These species, positioned on both barium and alumina sites, are very stable to high temperature. Nova et al. proposed that these isocyanates can serve as reaction intermediates for the reduction of NO_X using CO as reductant [39], and these species can react with the stored nitrates to form N_2. However, this reaction is relatively slow, since it is a solid–solid reaction where the diffusion can be a rate-limiting step. Szailer et al. [38] found that at 300 °C, although –NCO species had accumulated on the catalyst surface when using CO as the reductant, appreciable amounts of nitrates could still be detected by DRIFTS. As mentioned previously, it has been proposed that there are two types of barium species, those around Pt sites and those further away from Pt sites. It is very likely that NO_X stored around the Pt sites can react with CO to form –NCO. The reaction pathway can be described as CO spillover from Pt to barium sites, but not NO_X spillover to Pt sites, since it was found that most of –NCO species were associated with the barium sites. However, due to the limited mobility of the CO molecule, the reduction of barium nitrates away from Pt sites is less significant.

Although –NCO species are formed, this does not explain the NO_X release at the switch from the rich to lean phase. If –NCO species are formed and accumulate on the surface, they would act as an intermediate and react with NO in the lean phase, leading to NO_X elimination, not a NO_X release peak. To verify this, an experiment was designed as follows, with the results shown in Fig. 13(a) and (b): (1) store NO_X until saturation; (2) introduce CO to generate NCO species; (3) flush with N_2 to remove the CO; (4) introduce NO or O_2 and detect the reaction product. For comparison, a dashed line is included in Fig. 13(a), which represents outlet NO concentration data obtained when doing the same but with a clean surface (catalyst only reduced by H_2 in lieu of steps 1–3). For this clean surface, after NO introduction, breakthrough was observed very quickly, with a sharp NO concentration increase. By contrast, for the surface covered with –NCO, the NO concentration increased gradually (Fig. 13(a)), suggesting a slow reaction between NO and –NCO species. In addition, some N_2O is formed as a product, and it is expected that some N_2 was also formed.

The reactivity of –NCO species with O_2 is shown in Fig. 13(b). NO and NO_2 were immediately observed with the introduction of O_2, and appreciable amounts of N_2O were observed as well. This demonstrates that the –NCO species can be oxidized by O_2 to form NO_X. These results show that the NO_X release at the onset of the lean phase during cycling conditions is actually related to oxygen. It can be expected that most of the oxidized NO_X is adsorbed again by the barium sites in the form of nitrates, with only a small portion released due to the fast oxidation process. Literature evidence has suggested that the oxidation products of –NCO mainly consist of N_2, CO_2 as well as a small amount of N_2O, but not NO_X, for instance over an Ag/Al_2O_3 catalyst at 300 °C [40]. These results, however, demonstrate that at least some of the product can be NO_X, and this is possibly due to the higher relative oxidation activity of Pt.

In summary, the ineffectiveness of using dry CO as a reductant for stored NO_X is related to –NCO formation. First, due to the limited mobility of CO molecule, the reduction of nitrates is limited, and only the barium species around Pt can be reduced, with the formation of appreciable amounts of –NCO. Moreover, the reaction between NCO species and nitrates is very slow, due to the mass transfer limitation of the solid–solid reaction. Secondly, Ba poisoning by NCO can occur. Although nitrates can be reduced by CO into NCO in the rich phase, part of the NCO species can be oxidized by oxygen into NO_X and stored as nitrates again during the lean phase. Such a barium isocyanate–nitrate cycle makes part of the barium species, even around Pt sites, inactive for NO_X destruction.

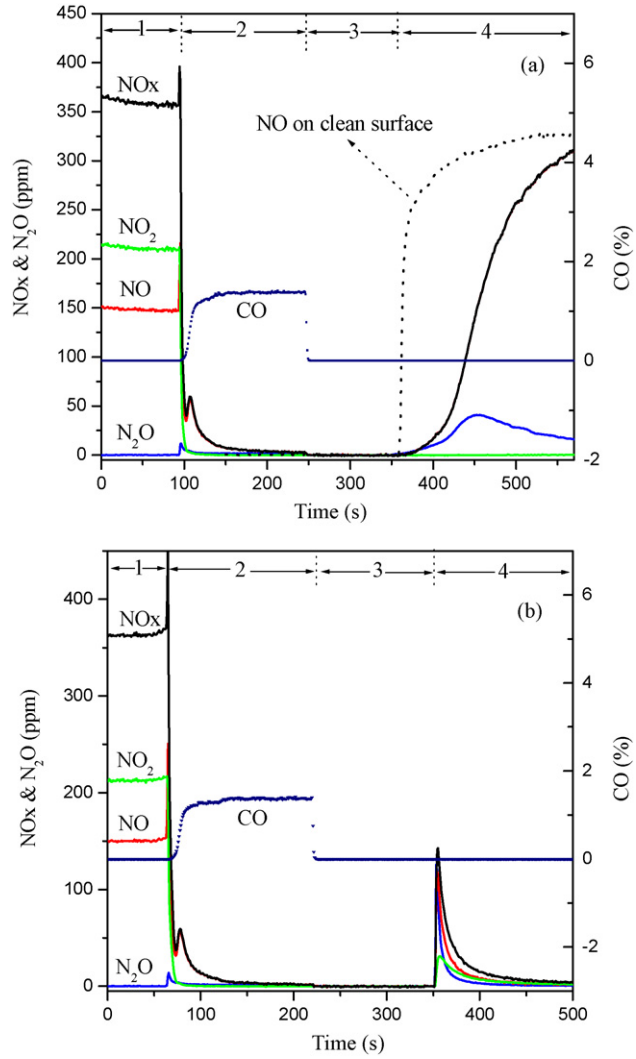

Fig. 13. Reactivity of NCO towards (a) NO and (b) O_2 at 350 °C. (1: NO_X storage to saturation in 360 ppm NO, 10% O_2; 2: 1% CO introduction to generate NCO; 3.N_2 purging; 4. introduction of 360 ppm NO or 10% O_2 for reaction.) For comparison purpose, the dotted line in panel (a) refers to introduction of NO on a H_2-reduced clean surface.

It is expected that this cycle plays an important role in the case of using dry CO as a reductant, as shown in Fig. 12(c). The substantial NO_X release at the beginning of the lean phase indicates that a large portion of the barium species is poisoned by the NCO species. After switching to the lean phase, the surface becomes covered by NO_X released from NCO oxidation, and the feed NO_X can be only stored by its slow diffusion from surface into the semi-bulk or bulk phase, or far from the Pt sites. This leads to the NO concentration remaining unchanged and NO_2 concentration gradually increasing since it is only NO_2 being trapped due to its ability to react with Ba sites not near Pt.

With this picture of the poisoning effect of CO, the promotional effect of H_2O becomes apparent. First, since the barium can be poisoned towards nitrate formation as a result of CO from the RWGS reaction, the presence of H_2O limits the reversible RWGS reaction and CO formation, weakening its detrimental effect. The formation of CO during cycling conditions is shown in Fig. 14. At 350 and 425 °C, the amounts of outlet CO formed were 36.1 and 146.7 μmol in the absence of H_2O, but were only 8.8 and 31.6 μmol in the presence of H_2O. H_2O decreases the amount of CO by more than 75%. Secondly, literature evidence suggests that the –NCO species are easily hydrolyzed [39]. The reactivity of –NCO species toward H_2O

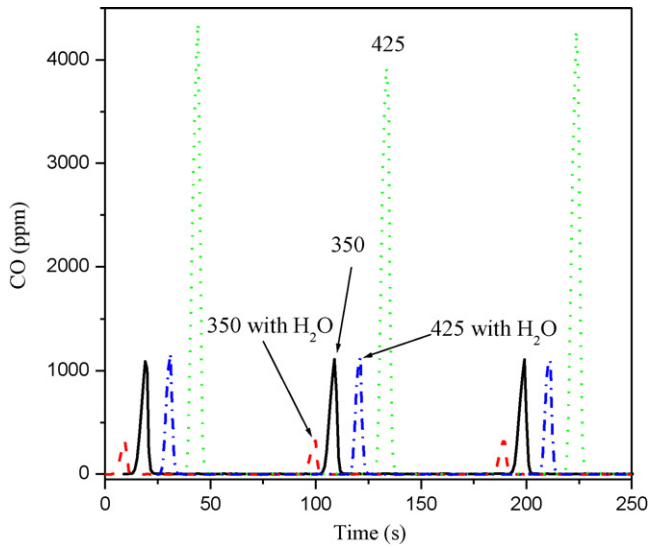

Fig. 14. CO outlet concentration profiles vs. time during three consecutive cycles at 350 and 425 °C with or without 5% H_2O (lean: 360 ppm NO, 10% O_2, 5% CO_2; rich: 1% H_2; balance N_2).

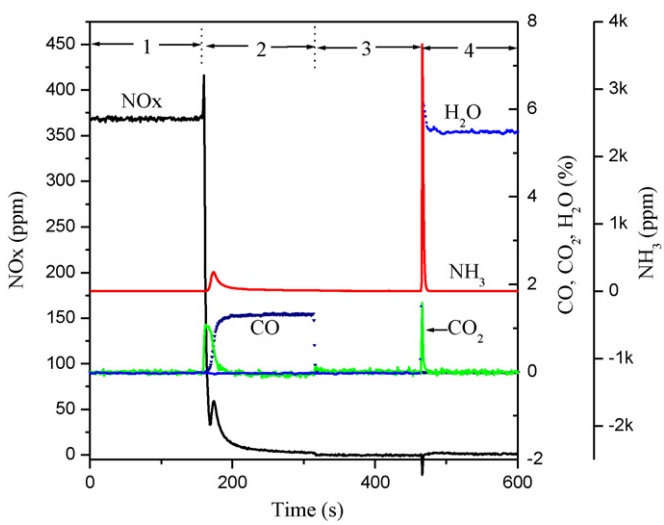

Fig. 15. Reactivity of NCO towards H_2O (same as Fig. 12 but introduce 5% H_2O in step 4).

was evaluated, and the results are shown in Fig. 15. Due to the hydrolysis of –NCO, large amounts of NH_3 and CO_2 were quickly formed as soon as H_2O was introduced. It is well known that NH_3 is as effective as H_2 as a reductant in NSR regeneration at relatively high temperature, such as 350 and 425 °C [28]. Therefore, high activity for NO_X destruction can be achieved in the presence of H_2O if –NCO species are formed. This is an important reason for CO being as effective as H_2 as a reductant at high temperature. The water–gas shift reaction can also lead to H_2 and then its use as a reductant [9,12], but the NCO route cannot be excluded. When H_2 is used as the reductant, if CO_2 is present, the reaction between CO from the RWGS reaction and surface nitrates still exists. Although H_2O can be formed at the same time, it appears that it is not enough to hydrolyze all the –NCO species. Even in the presence of 5% H_2O, trace amounts of –NCO are still present on the surface at 350 °C, as indicated by a small characteristic NO_X release peak at the onset of the lean phase. However, at 425 °C such a peak is not evident indicating complete hydrolysis or absence of –NCO. As a result, compared with 350 °C, a slightly higher promotional effect of H_2O was observed at 425 °C.

In summary, the surface chemistry can be expressed as the following reactions, and it is apparent that H_2O always drives the reaction toward H_2 or NH_3, both of which are highly active reductants.

$$H_2 + CO_2 \leftrightarrow H_2O + CO; \quad (1)$$

$$4CO + NO_3^- \rightarrow NCO^- + 3CO_2; \quad (2)$$

$$NCO^- + 2H_2O \rightarrow CO_2 + NH_3 + OH^-. \quad (3)$$

4. Conclusion

A detailed investigation of the effect of H_2O on the performance of NO_X storage and reduction over a model $Pt/Ba/Al_2O_3$ catalyst was performed using H_2 as the reductant, both in the presence and absence of H_2O and/or CO_2. In the absence of CO_2, regeneration is the rate-determining step in the cycle at low temperature, and it is accomplished by spillover of hydrogen, activated on Pt sites, to barium nitrates, but not the reverse migration of nitrates to Pt sites. The hydrogen spillover rate over the support limits the regeneration rate. If H_2O is present, surface hydroxyl groups are formed and stabilized, and serve as a "bucket brigade" for fast transport of the spillover hydrogen, facilitating more extensive regeneration. At high temperature, NO_X storage determines the performance. Since H_2O can decrease the NO_X storage capacity, its addition slightly decreases the performance.

In the presence of CO_2, addition of H_2O promoted NO_X conversion over the entire temperature range tested. CO formed from the RWGS reaction can limit regeneration or even poison the catalyst, and the poisoning mechanism can be attributed to the unfavorable cycle between barium isocyanates and nitrates, since the former can be quickly oxidized by O_2 in the lean phase to NO_X, which is adsorbed on the barium sites again as nitrates, making part of the barium sites, even around Pt, inactive for further NO_X trapping. The presence of H_2O greatly decreases the detrimental effect of CO. First, it suppresses the RWGS reaction and the subsequent poisoning effect of CO. Secondly, if NCO is formed by CO, it can be quickly hydrolyzed by H_2O into NH_3, which is an efficient reductant in the NSR cycle.

Acknowledgements

The authors would like to thank the Natural Sciences and Engineering Research Council of Canada for funding this work and Johnson Matthey for the sample provided.

References

[1] W.S. Epling, L.E. Campbell, A. Yezerets, N.W. Currier, J.E. Parks, Catal. Rev. 46 (2004) 163.
[2] L. Lietti, P. Forzatti, I. Nova, E. Tronconi, J. Catal. 204 (2001) 175.
[3] W.S. Epling, J.E. Parks, G.C. Campbell, A. Yezerets, N.W. Currier, L.E. Campbell, Catal. Today 96 (2004) 21.
[4] W.S. Epling, G.C. Campbell, J.E. Parks, Catal. Lett. 90 (2003) 45.
[5] C.M.L. Scholz, V.R. Gangwal, M.H.J.M. de Croon, J.C. Schouten, Appl. Catal. B 71 (2007) 143.
[6] E.C. Corbos, X. Courtois, N. Bion, P. Marecot, D. Duprez, Appl. Catal. B 76 (2007) 357.
[7] A. Lindholm, N.W. Currier, E. Fridell, A. Yezerets, L. Olsson, Appl. Catal. B 75 (2007) 78.
[8] S.S. Chaugule, A. Yezerets, N.W. Currier, F.H. Ribeiro, W.N. Deglass, Catal. Today, in press, doi:10.1016/j.cattod.2010.02.024.
[9] N. Takahashi, K. Yamazaki, H. Sobukawa, H. Shinjoh, App. Catal. B 70 (2007) 198.
[10] M. AL-Harbi, W.S. Epling, Appl. Catal. B 89 (2009) 315.
[11] H. Abdulhamid, J. Dawody, E. Fridell, M. Skoglundh, J. Catal. 244 (2006) 169.
[12] J. Theis, H.W. Jen, R. McCabe, M. Sharma, V. Balakotaiah, M.P. Harold, SAE paper no 2006-01-1067.
[13] L. Lietti, I. Nova, P. Forzatti, J. Catal. 257 (2008) 270.

[14] A. Lindholm, N.W. Currier, J. Li, A. Yezerets, L. Olsson, J. Catal. 258 (2008) 273.
[15] C.M.L. Scholz, V.R. Gangwal, M.H.J.M. de Croon, J.C. Schouten, J. Catal. 245 (2007) 215.
[16] W.S. Epling, D. kisinger, C. Everest, Catal. Today 136 (2008) 156.
[17] I. Nova, L. Lietti, L. Castoldi, E. Tronconi, P. Forzatti, J. Catal. 239 (2006) 244.
[18] I. Nova, L. Lietti, P. Forzatti, Catal. Today 136 (2008) 128.
[19] E. Fridell, M. Skoglundh, B. Westerberg, S. Johansson, G. Smedler, J. Catal. 183 (1999) 196.
[20] R.D. Clayton, M.P. Harold, V. Balakotaiah, AICHE J. 55 (2009) 687.
[21] L. Xu, R. McCabe, W. Ruona, G. Cavataio, SAE paper no 2009-01-0285.
[22] L. Olsson, M. Abul-Milh, H. Karlsson, E. Jobson, P. Thormahlen, A. Hinz, Top. Catal. 30 (31) (2004) 85.
[23] G.W. Graham, H.W. Jen, J.R. Theis, R.W. McCabe, Catal. Lett. 93 (2004) 3.
[24] D.H. Kim, Y.H. Chin, J.H. Kwak, C.H.F. Peden, Catal. Lett. 124 (2008) 39.
[25] Y. Ji, T.J. Toops, J.A. Phil, M. Crocker, Appl. Catal. B 91 (2009) 329.
[26] G. Zhou, T. Luo, R.J. Gorte, Appl. Catal. B 64 (2006) 88.
[27] D. James, E. Fourrem, M. Ishii, M. Bowker, Appl. Catal. B 45 (2003) 147.
[28] L. Cumaranatunge, S.S. Mulla, A. Yezerets, N.W. Currier, W.N. Delgass, F.H. Ribeiro, J. Catal. 246 (2007) 29.
[29] J.Y. Luo, M. Meng, X. Li, X.G. Li, Y.Q. Zha, T.D. Hu, Y.N. Xie, J. Zhang, J. Catal. 254 (2008) 310.
[30] M. Meng, Y.Q. Zha, J.Y. Luo, T.D. Hu, Y.N. Xie, T. Liu, J. Zhang, Appl. Catal. A 301 (2006) 145.
[31] R.D. Clayton, M.P. Harold, V. Balakotaiah, C.Z. Wan, Appl. Catal. B 90 (2009) 662.
[32] W.C. Conner Jr., J.L. Falconer, Chem. Rev. 95 (1995) 759.
[33] R.B. Levy, M. Boudart, J. Catal. 32 (1974) 304.
[34] J. Szanyi, J.H. Kwak, R.J. Chimentao, C.H.F. Peden, J. Phys. Chem. C 111 (2007) 2661.
[35] L. Olsson, P. Jozsa, M. Nilsson, E. Jobson, Top. Catal. 42 (42) (2007) 95.
[36] S. Balcon, C. Potvin, L. Salin, J.F. Tempere, G.D. Mariadassou, Catal. Lett. 60 (1999) 39.
[37] J.P. Breen, R. Burch, C.F. Gautrelet, C. Hardacre, C. Rioche, Appl. Catal. B 81 (2008) 150.
[38] T. Szailer, J.H. Kwak, D.H. Kim, J.C. Hanson, C.H.F. Peden, J. Szanyi, J. Catal. 239 (2006) 51.
[39] L. Nova, L. Lietti, P. Forzatti, F. Frola, F. Prinetto, G. Ghiotti, Top. Catal. 52 (2009) 1757.
[40] N. Bion, J. Saussey, M. Haneda, M. Daturi, J. Catal. 217 (2003) 47.